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Fundamental and Applied Aspects of
Physical Chemistry*

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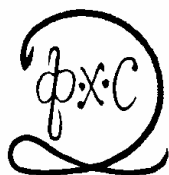
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INTRAPARTICLE DIFFUSION AND ADSORPTION OF HEAVY METALS ONTO POROUS POLYMER

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ABSTRACT

Intraparticle diffusion kinetic model (IPD) was used to elucidate the influence of macroporous glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA) copolymer (PGME) with attached diethylene triamine (PGME-deta) on the competitive Cu(II), Cd(II), Co(II) and Ni(II) ions sorption from aqueous solutions. Surface sorption was examined by SEM-EDS analysis.

INTRODUCTION

Copper, cadmium, cobalt and nickel (Co, Cd, Co and Ni) are among the most common pollutants in industrial effluents [1]. Chronic exposure to high Cd levels causes renal dysfunction, bone degeneration, liver and blood damage. Co and Ni cause skin rashes, asthma, allergies, pneumonia, etc. Cu can also be toxic, even at very low concentrations. The EPA requires Cu and Cd levels in drinking water not to exceed 1.3 and 0.005 mg L⁻¹, respectively [2]. Maximum permitted levels in drinking water for Cu, Ni and Cd in Republic of Serbia are 2.0, 0.02 and 0.003 mg L⁻¹ [3]. Polymeric adsorbents have been frequently used for heavy metals removal from aqueous solutions. Amino-functionalized macroporous PGME has high capacity and good selectivity for the precious and heavy metal ions over alkali and alkaline earth metals [4]. Depending on pH, it can coordinate heavy and precious metals or bind them as chloro complexes [5].

EXPERIMENTAL

Macroporous PGME was prepared by free-radical suspension polymerization of GMA and EGDMA thermally initiated by decomposition of 2,2'-azobis (isobutyronitrile) (AIBN) as the source of radicals in the

presence of inert component (cyclohexanol and hexadecanol) [6]. The copolymerization was carried out at 70 °C for 2 h and at 80 °C for 6 h with a stirring rate of 200 rpm. PGME sample was purified with ethanol, additionally functionalized with diethylene triamine and labeled as PGME-10/16-deta. Specific pore volume (0.66 cm³), pore diameter (60 nm) which corresponds to half of pore volume and specific surface area (50 m² g⁻¹), of PGME-10/16-deta were determined by mercury porosimetry (Carlo Erba 2000, software Milestone 200). SEM-EDS (energy-dispersive X-ray spectroscopy) analysis was performed on Jeol JSM 5800 instrument operating at 20 kV. The amino group concentration calculated from elemental analysis was $C_{AG}=4.9$ mmol g⁻¹. Sorption of metal ions was investigated under batch competitive conditions. PGME (0.5 g) was contacted with 50 cm³ of mixed metal salt solution ($C_i=0.05$ M, pH=5.0, $t=180$ min, $T=298$ K). The concentration of Cu(II), Cd(II), Co(II) and Ni(II) ions in the aqueous phases was determined by atomic absorption spectrometry (AAS, SpektrAA Varian Instruments). The sorption capacity (Q_t , mmol g⁻¹) at any time t , was calculated from:

$$Q_t = \frac{(C_i - C_t)V}{m} \quad (1)$$

Where: C_i and C_t are concentrations of metal ions in the initial solution and in aqueous solution at time t (min), V is the volume of the aqueous phase (dm³) and m is the mass of the sorbent particles (g).

RESULTS AND DISCUSSION

Previous study showed that the maximum sorption capacities of PGME-10/16-deta under competitive conditions were 1.18 mmol g⁻¹ for Cu(II), 0.67 mmol g⁻¹ for Cd(II), 0.24 mmol g⁻¹ for Co(II) and 0.23 mmol g⁻¹ for Ni(II) ions [4].

For the sake of additional understanding of Cu(II), Cd(II), Co(II) and Ni(II) ions sorption, the surface of PGME-10/16-deta particles with sorbed metal ions was examined by SEM-EDS analysis. The results are presented in Figure 1 and Table 1.

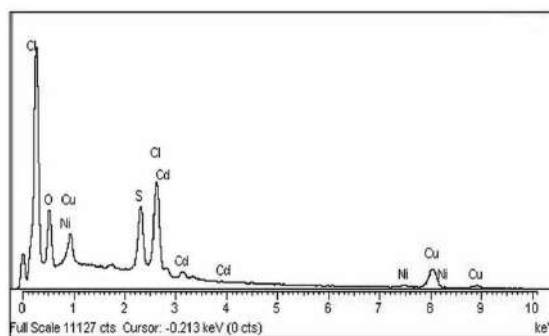


Figure 1. EDS spectra of PGME-10/16-deta with sorbed heavy metal ions.

As expected, EDS analysis confirmed that amount of metal ions bounded to the amino groups on the particle surface decreased in the order: Cu(II) >> Cd(II) > Ni(II) ions. Previously, it was established that Cu(II), Cd(II), Co(II) and Ni(II) ions sorption under competitive conditions obeys pseudo-second order (PSO) kinetics [4]. Namely, the coefficients of determination (R^2) for the PSO kinetics model were closer to unity in comparison to the corresponding R^2 values for PFO kinetics. Also, the experimental equilibrium capacity (Q_e^{exp}) values were almost identical to the values calculated (Q_e^{calc}) using PSO kinetics model, indicating that the sorption rate is controlled by both the sorbent capacity and the sorbate concentration.

In this study, intraparticle (IPD) model was applied to determine whether the process rate in the studied sorption system is directed by film and/or pore diffusion [7, 8]:

Table 1. SEM-EDS analysis of PGME-10/16-deta with sorbed heavy metal ions

Element	Mass. %	Atomic %
O K	54.68	76.40
S K	9.71	6.77
Cl K	17.45	11.00
Ni K	0.98	0.37
Cu K	13.34	4.69
Cd L	3.84	0.76

$$Q_t = k_{id}t^{1/2} + C_{id} \quad (2)$$

where k_{id} is the intraparticle diffusion coefficient and C_{id} is a constant related to the thickness of the boundary layer.

IPD ($Q_t - t^{1/2}$) plots for the Cu(II), Cd(II), Co(II) and Ni(II) ions sorption are given in Figure 2. The maximal sorption capacities and kinetic parameters calculated from

IPD kinetic model are presented in Table 2.

According to the literature, multilinear IPD plots observed in Fig. 2 might represent the stages of sorbate sorption into the macro-, meso, and microporous structure of sorbent [8,9]. The first and the fastest stage of heavy metal ions sorption can be ascribed to the sorption over the external surface and in the macropores of PGME-deta, the second to the IPD through mesopores, while the third could be regarded as the diffusion through micropores, and achieving the equilibrium.

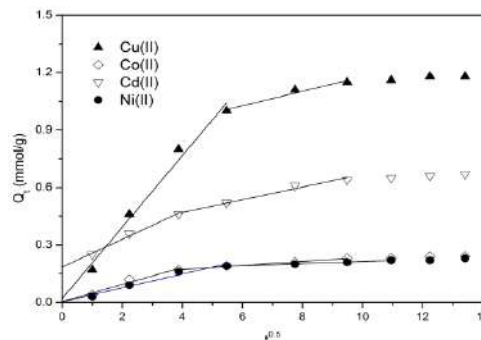


Figure 2. Plots of IPD model for competitive Cu(II), Cd(II), Co(II) and Ni(II) ions sorption on PGME-10/16-deta.

Table 2. Kinetic parameters for Cu(II), Cd(II), Co(II) and Ni(II) ions sorption using PGME-10/16-deta calculated from IPD kinetic model.

Intraparticle diffusion	Metal ions			
	Co(II)	Cd(II)	Cu(II)	Ni(II)
k_{1id} , mmol/(g min ^{0.5})	0.045	0.073	0.187	0.036
C_{1id} , mmol/g	0.005	0.186	0.020	0.004
R^2	0.955	0.988	0.983	0.966
K_{2id} , mmol/(g min ^{0.5})	0.010	0.033	0.038	0.005
C_{2id} , mmol/g	0.131	0.338	0.799	0.159
R^2	0.996	0.979	0.965	0.990

CONCLUSION

Kinetics of competitive Cu(II), Cd(II), Co(II) and Ni(II) ions sorption from aqueous solutions by macroporous PGME-deta was analyzed using intraparticle diffusion (IPD) kinetic model. The analysis revealed that pore diffusion was the only rate-controlling step in the process of heavy metal sorption by the porous copolymer.

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